

"Slater Wave Functions
for the
Valence Electrons
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Quadrivalent Carbon"
by
Paul Alexander Puhach

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"Slater Wave Functions
for the
Valence Electrons
of
Quadrivalent Carbon"

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

by

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September, 1953

SLATER WAVE FUNCTIONS FOR THE VALENCE ELECTRONS OF QUADRIVALENT CARBON

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ABSTRACT

The meaning of and need for a "unipotential" for the valence electrons of an atom are presented, with a treatment of an ad hoc proposition due to J. C. Slater for such a potential.

The Hartree-Fock field for the configuration $1s^2 2s^2 2p^3$ of carbon is evaluated from radial distribution amplitudes given by A. Jucys, and tabulated in such a manner as to facilitate unipotential calculations. The first phase of a self-consistent calculation on Slater's unipotential is then effected.

The accuracy and immediate applicability of the resulting radial distribution amplitudes are then discussed.

Glossary of Symbols not Defined in the Text, in Order of First Appearance

Page	Section	Symbol	Definition
1	1	∇_k^2	The Laplacian operator with respect to coordinates (k); $= \partial^2/\partial x_k^2 + \partial^2/\partial y_k^2 + \partial^2/\partial z_k^2$
1	1	Z	Atomic number; for carbon, 6.
1	1	$u_j(k)$	Atomic orbital for electron in state j with coordinates (k) $\rightarrow r_k \theta_k \phi_k s_k$ or $x_k y_k z_k s_k$; $= P(n\ell_j r_k) S(\ell_j m_j \theta_k \phi_k) \alpha(s_j s_k) / r_k$, where $P(n\ell_j r_k)$ is the radial distribution amplitude; $S(\ell_j m_j \theta_k \phi_k)$ is the spherical harmonic part; $\alpha(s_j s_k)$ is the spin factor; and the quantum numbers have the usual significance.
1	1	r_{12}	$= [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$
1	1	$E_i = E_{n_i \ell_i}$	The energy parameter of the equation for the <u>i</u> th orbital.
2	1	$W(1)=W(r_1)$	The Slater exchange potential.
3	1	$R_{n\ell}(r)$	$= P(n\ell r) / r$.
4	2	$Y_k(n\ell, n'\ell'; r)$	$= \frac{1}{r^k} \int_0^r dr P(n\ell r) P(n'\ell' r) r^k + r^{kd} \int_r^\infty dr P(n\ell r) P(n'\ell' r) / r^{kd}$
8	4	δ	Central difference operator.
Appendix II		$P_n^m(\zeta)$	Associated Legendre polynomials.

1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation

$$f(x) = \int_0^x \frac{1}{1+t^2} dt$$

It is shown that the function $f(x)$ is continuous and differentiable on the interval $(-\infty, \infty)$. The derivative of the function is given by the formula

$$f'(x) = \frac{1}{1+x^2}$$

It is also shown that the function $f(x)$ is bounded on the interval $(-\infty, \infty)$. The maximum and minimum values of the function are given by the formulas

$$\max_{x \in (-\infty, \infty)} f(x) = \frac{\pi}{2}, \quad \min_{x \in (-\infty, \infty)} f(x) = -\frac{\pi}{2}$$

The function $f(x)$ is also shown to be concave up on the interval $(-\infty, \infty)$. The concavity of the function is given by the formula

$$f''(x) = -\frac{2x}{(1+x^2)^2}$$

Finally, it is shown that the function $f(x)$ is periodic with period π . The periodicity of the function is given by the formula

$$f(x+\pi) = f(x) + \pi$$

1. Introduction--A number of approximation methods have been applied to the many-body problem in quantum mechanics. The most accurate one-electron method is that of Hartree and Fock (v. Appendix I), which includes the Pauli principle in its framework, and as a mathematical consequence supposes the individual electrons to move in potential fields which are not the same for all. Work in the band theory of solids and problems in molecular binding, etc., requires wave functions arising from a potential field which is the same for all electrons--a "unipotential"--if calculations are to be practicable. J. C. Slater has proposed ad hoc an averaging process to be applied to the Hartree-Fock field¹ in hopes of retaining the accuracy of the Hartree-Fock method while accruing unipotential simplicity.

In this thesis, the Hartree-Fock field is evaluated for the configuration $1s^2 2s 2p^3$; ⁵S of carbon from wave functions given by A. Jucys² and is tabulated in such a manner as to facilitate calculation of unipotentials, Slater's and others.³ The first phase of a self-consistent calculation is then carried out using Slater's unipotential; the set of wave functions for the valence electrons which obtains differs little from Jucys'.

The Hartree-Fock equations have been modified for tractability by Dirac⁴ and Slater;¹ for an atomic system the modified equations read:

$$1.1 \left[-\frac{1}{2} \nabla^2 - \frac{Z}{r_i} + \sum_{j=1}^Z \int d\tau_2 \frac{u_j^*(2)}{r_{12}} \frac{1}{r_{12}} u_j(2) - \sum_{j=1}^Z \int d\tau_2 \frac{u_j^*(1) u_j^*(2) u_j(1) u_j(2)}{r_{12} |u_i(1)|^2} \right] u_i(1) = E_i u_i(1)$$

(cf. Appendix I), where (1) represents the coordinates, including spin, of the electron in the ith state, and (2) the corresponding umbral variables of integration; the integral sign implies summation over spin. In the literature, the first summation is called the Coulomb term of the potential, while the second is usually designated the exchange term. Hartree

1. J. C. Slater, Phys. Rev., 81, 385, '51.

2. A. Jucys, J. Phys. USSR, XI, #1, '47.

3. R. T. Sharp and G. K. Horton, Phys. Rev., 90, 317, '53.

4. P. A. M. Dirac, Proc. Camb. Phil. Soc., 26, 376, '30.

⁵
units are used here and throughout this thesis.

Only the exchange term of 1.1 is not the same for all electrons. In the case of the 1s electrons of quadrivalent carbon, this non-uniformity is not an objection in the sense of paragraph one above, for the K electrons are not involved in interaction calculations. (Moreover, self-consistent calculations for the beryllium atom and ions and for the carbon atom have shown the core electrons to be insensitive to the presence of other electrons⁶ and to exchange effects,⁷ so that for this work, the radial part of the 1s wave functions may be taken as that given by either Jucys² or ^{C.}Torrance⁷; the difference is at most .002.) For the valence electrons, however, the exchange must be rendered uniform; this was accomplished by Slater's method. While the above procedure amounts to calculating the 1s and 2s radial parts from different potentials, the objection that they will no longer be orthogonal is not serious in practice; the error introduced by ignoring the defect from orthogonality (as it turns out, a small defect) is probably obscured by the intrinsic inaccuracy of the approximate theory under consideration: moreover, one of the 1s orbitals is orthogonal to the 2s orbital because of opposed spin.

The exchange appropriate to the valence electrons is shown in Appendix I to be:

$$1.2 \quad W(1) = \sum_i \sum_{j=1}^Z \int d\tau_2 u_i^*(1) u_j^*(2) \frac{1}{r_{12}} u_i(2) u_j(1) / \sum_i u_i^*(1) u_i(1)$$

where the i summation is over valence electrons only.

In order that equation 1.1 and its counterpart with exchange 1.2 shall be separable, the potential must be assumed spherically symmetrical.

5. D.Hartree, Proc. Roy. Soc., 141, 282, '33.

6. D. R. and W. Hartree, Proc. Roy. Soc., A154, 588, '36.

7. C.Torrance, Phys. Rev., 46, 388, '34.

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Fortuitously, this condition is met by the aggregate integrands of the Coulomb term for quadrivalent carbon; where angular dependence arose in the exchange it was suppressed by an averaging process effected by multiplying by $d\theta, d\varphi, \sin\theta$, and integrating over all angles.

The assumption of a spherically symmetrical potential gives rise to the usual spherical harmonics for the angular parts of the $u_\ell(\vec{r})$; only the radial equation need be solved. This reads:

$$-\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} R_{n\ell} \right) - \frac{\ell(\ell+1)}{r^2} R_{n\ell} + 2 [E_{n\ell} - V] R_{n\ell} = 0,$$

where $V(r)$ includes the appropriate exchange term. Under the transformation $P(n\ell|r) = r R_{n\ell}(r)$, the radial equation becomes

$$1.3 \quad \frac{d^2}{dr^2} P(n\ell|r) = \left[\frac{\ell(\ell+1)}{r^2} - 2(E_{n\ell} - V) \right] P(n\ell|r).$$

2. Evaluation of the Coulomb and Exchange Terms--To facilitate manipulation of the integrals appearing in the Coulomb and exchange terms, indices were assigned to the states occupied by the electrons in the configuration $1s^2 2s 2p^3$ as follows.

Index	Electronic State $n l m m_s$
1	1 0 0 $\frac{1}{2}$
2	1 0 0 $-\frac{1}{2}$
3	2 0 0 $\frac{1}{2}$
4	2 1 1 $\frac{1}{2}$
5	2 1 0 $\frac{1}{2}$
6	2 1 -1 $\frac{1}{2}$

The integrals

$$2.1 \quad I_k = \int d\tau_2 u_k^*(2) \frac{1}{r_{12}} u_k(2)$$

and

$$2.2 \quad I_{jk} = \int d\tau_2 u_j^*(1) u_k^*(2) \frac{1}{r_{12}} u_k(1) u_j(2),$$

called respectively the Coulomb and exchange integrals, were reduced to single integrations over the variable r_2 . The details are given in Appendix II, where I_{16} is worked out, since it exemplifies all the peculiarities encountered, including angular dependence.

Expressions follow for the various integrals, averaging over angles having been effected where necessary. Integrals of the form $I_{j2} = I_{2j}$, $j \neq 2$, vanish because of opposed spin.

The Coulomb term, as evaluated by the method of Appendix II is

$$2.3 \quad I(r) = \sum_{j=1}^6 I_j = \frac{1}{r} \left[2Y_0(1s, 1s; r) + Y_0(2s, 2s; r) + 3Y_0(2p, 2p; r) \right]$$

The exchange integrals are given by:

$$\begin{aligned} 2.4 \quad I_{33} &= P^2(2s|r)Y_0(2s, 2s; r)/4\pi r^3; \\ I_{44} &= P^2(2p|r) \left[Y_0(2p, 2p; r) + \frac{1}{25}Y_2(2p, 2p; r) \right] / 4\pi r^3, \\ &= I_{44}; \\ I_{55} &= P^2(2p|r) \left[Y_0(2p, 2p; r) + \frac{4}{25}Y_2(2p, 2p; r) \right] / 4\pi r^3, \\ I_{13} &= P(1s|r)P(2s|r)Y_0(1s, 2s; r)/4\pi r^3; \\ I_{14} &= P(1s|r)P(2p|r)Y_1(1s, 2p; r)/12\pi r^3, \\ &= I_{15} = I_{16}; \\ I_{34} &= P(2s|r)P(2p|r) \left[Y_1(2s, 2p; r) \right] / 12\pi r^3, \\ &= I_{35} = I_{36}; \\ I_{45} &= 3P^2(2p|r)Y_2(2p, 2p; r)/100\pi r^3, \\ &= \frac{1}{2}I_{46} = I_{56}. \end{aligned}$$

The foregoing were evaluated numerically from Jucys' wave functions² by the following method. Let $f(r)$ be an integrand tabulated at intervals h of the argument; then integrals of the form $\int_0^{2kh} f(r)dr$ were evaluated by Simpson's rule, where k is an integer. The integral $\int_0^{4h} f(r)dr$ was then calculated by Cotes' three-eighths rule, whereupon $\int_0^h f(r)dr = \int_0^{4h} f(r)dr - \int_h^{4h} f(r)dr$ was found. To complete evaluation of the integral up to all tabular values of r , integrals of the form $\int_{(2k+1)h}^{(2k+3)h} f(r)dr$ were computed by Simpson's rule.

$I(r)$ as given by 2.3 is tabulated in Table I, as ^{are} the combinations

$$B(r) = 4\pi(I_{1,3} + I_{2,3} + I_{3,4} + I_{3,5} + I_{4,5})$$

and

$$C(r) = 4\pi(I_{1,4} + I_{1,5} + I_{2,4} + I_{2,5} + I_{3,4} + I_{3,5} + I_{4,4} + I_{4,5} + I_{5,4} + I_{5,5} + I_{6,4} + I_{6,5})$$

which lend themselves to calculation of the unipotential in this and other problems.³

As shown in Appendix I,

$$2.5 \quad W(r) = [B(r) + C(r)] / r^2 [P^2(2s|r) + 3P^2(2p|r)] ;$$

this expression is also tabulated in Table I.

Plots of $I(r)$ and $W(r)$ vs. r are given in Fig. I.

3. Solutions of the Radial Equation for Small and Large r --Equation 1.3⁷ may be written

$$3.1 \quad d^2 P(n\ell|r) / dr^2 = \left[\ell(\ell+1) / r^2 - 2\mathcal{E}/r + 2(I - W) + 2|E_{n\ell}| \right] P(n\ell|r) .$$

(a) In order to obtain a working approximation to the solutions of 3.1 in the vicinity of the origin, a cubic curve was fitted to four consecutive values of $(I - W)$, starting with the second from the origin, by means of Lagrange's interpolation formula.⁸ For $F(r) \equiv (I - W) = a + br + cr^2 + dr^3$, Lagrange's interpolation formula yields:

$$\begin{aligned} a &= -\frac{1}{6}(r_1 r_2 r_3 F_4 - F_1 r_2 r_3 r_4) - \frac{1}{2}(F_2 r_1 r_3 r_4 - F_3 r_1 r_2 r_4), \\ b &= \frac{1}{6} \left[F_4(r_1 r_2 + r_3 r_1 + r_2 r_3) - F_1(r_2 r_3 + r_2 r_4 + r_3 r_4) \right] - \frac{1}{2} \left[F_2(r_1 r_3 + r_1 r_4 + r_3 r_4) - F_3(r_1 r_2 + r_1 r_4 + r_2 r_4) \right] \\ c &= -\frac{1}{6} \left[F_1(r_2 + r_3 + r_4) - F_4(r_1 + r_2 + r_3) \right] - \frac{1}{2} \left[F_3(r_1 + r_2 + r_4) - F_2(r_1 + r_3 + r_4) \right] \\ d &= \frac{1}{6}(F_4 - F_1) - \frac{1}{2}(F_2 - F_3), \end{aligned}$$

where $F(r_1) = F_1$, and $r_1 = .02$, $r_2 = .04$, etc.

Equation 3.1 may now be written in the form

$$3.2 \quad d^2 P / dr^2 + (\alpha/r^2 + \beta/r + \gamma + \delta r + \epsilon r^2 + \zeta r^3) P = 0; \quad (r \leq 0.08)$$

here $\alpha = -\ell(\ell+1)$, $\beta = 2\mathcal{E} = 12$, and γ is a augmented by $2|E_{n\ell}|$. This equation was solved by Frobenius' method; writing

8. H. Jeffreys and Jeffreys, Methods of Mathematical Physics, p. 327. (Cambridge University Press, England, 1946.)

$$e + \dots + \dots + \dots + \dots + \dots + \dots = \dots$$

... ..

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3.3

$$P = \sum_{\nu=0}^{\infty} a_{\nu} r^{\nu+\mu}; \quad (\mu > 0, \text{ since } P(n\ell|0) = 0),$$

and substituting into 3.2 yields recursion formulae for the a_{ν} by means of which two ordinates for purposes of starting numerical solutions outward from the origin were calculated. In Table II are given the a_{ν} from which starting ordinates for the final solutions were calculated; it is indicative of the insensitivity of the solution to changes in $|E_{n\ell}|$ (in the vicinity of the origin) that while the a_{ν} changed with changes in $|E_{n\ell}|$ the ordinates $P(n\ell|.02)$ and $P(n\ell|.04)$ did not.

Since the series 3.3 is certainly convergent as a consequence of the regularity of the differential equation of which it is a solution⁹, and, as it turns out, alternating, truncation error is smaller in absolute value than the first neglected or last counted term.

(b) By Table I, for $r \geq 6.0$, $I(r) \doteq 6/r$, and $W(r) \doteq 1/r$, so that 3.1 may be written

$$d^2 P(n\ell|r)/dr^2 = \left[\ell(\ell+1)/r^2 - 2/r + 2|E_{n\ell}| \right] P(n\ell|r), \quad r \geq 6.0;$$

this equation is soluble in terms of confluent hypergeometric functions: asymptotic expansions valid for large r are¹⁰

3.4

$$\begin{aligned} P(2s|r) &\sim A e^{-r/K} r^K \left\{ 1 + \frac{1/4 - (K - \frac{1}{2})^2}{1! 2r/K} + \dots \right\}, \quad K = \frac{1}{\sqrt{2|E_{2s}|}}, \\ P(2p|r) &\sim A e^{-r/K} r^K \left\{ 1 + \frac{3/4 - (K - \frac{1}{2})^2}{1! 2r/K} + \dots \right\}, \quad K = \frac{1}{\sqrt{2|E_{2p}|}} \end{aligned}$$

Table II gives numerical values for the various constants. These expressions were used to calculate starting ordinates for the inward numerical solutions dealt with in section 4 below.

4. Numerical Solution of the Radial Equation--The physically significant solutions of 3.1 result from choosing a value of the energy eigenvalue $E_{n\ell}$ which yields a "well-behaved" solution, i.e., a solution which approaches zero with a slope decreasing in absolute value for large r . The

9. E. Whittaker and G. Watson, Modern Analysis, p.199.

10. Whittaker and Watson, Ibidem, p. 337 ff.

(Cambridge University Press, England, 1946.)

The American Medical Association is a non-profit corporation organized for the purpose of promoting the interests of the medical profession and the public health. It was founded in 1847 and has since that time been the leading organization of the medical profession in this country. The Association is composed of more than 50,000 members, who are physicians, surgeons, dentists, and other medical practitioners. The Association's principal activities are the publication of the Journal of the American Medical Association, the holding of annual conventions, and the representation of the medical profession in legislative and executive bodies. The Association is also engaged in a wide variety of other activities, including the promotion of medical research, the improvement of medical education, and the advancement of the public health.

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asymptotic expansions 3.4 certainly meet this last requirement. Evaluation of the eigenvalue was accomplished by the method used by the Hartrees¹¹ for a given estimate of E_{nl} , numerical solutions of 3.1 were computed from the origin outward, and from $r = 6.5$ inward, using for a start ordinates computed by the methods of section 3; if the solutions could be made to merge smoothly (in the vicinity of $r = 3.5$), then the eigenvalue was adjudged correct. "Smoothness" was judged on this criterion: ordinates were calculated from each solution for $r = 3.5$ and $r = 4.0$; if the respective ordinates could be rendered equal (within estimated error) for both of these abscissae by the same numerical factor, then junction was considered smooth. Tables IV and V show that confluence within a few units in the fifth decimal place was obtained.

(The choice of $r = 3.5$ as the abscissa of confluence was dictated by the intervals in the tables of $I(r)$ and $W(r)$; fortuitously, it developed that the estimated cumulative errors due to truncation of a difference series used in the solution were of the same sign and order of magnitude there.)

To implement numerical solution, equation 3.1 was written

$$4.1 \quad d^2 P(n\ell|r)/dr^2 = g_{n\ell}(r)P(n\ell|r),$$

with $g_{n\ell}(r) = \ell(\ell+1)/r^2 - 2Z/r + 2(I - W) + 2|E_{n\ell}|$. The function $g_{n\ell}$ was calculated using the functions appearing in Table I, and tabulated; the final values of $g_{n\ell}$ are tabulated in Tables IV and V, incidentally to demonstrating the method of solution of 4.1 for the 2s and 2p cases respectively.

The method of solving 4.1 used is described by Jeffreys and Jeffreys.¹² By definition of the second central difference

11. Hartree and Hartree, Proc. Roy. Soc., A154, 588, '36

12. Jeffreys and Jeffreys, op. cit., p. 267 ff.

$$\begin{aligned}\delta^2 P(r) &= P(r+h) - 2P(r) + P(r-h) \\ &= (e^{hD} - 2 + e^{-hD})P(r) \\ &= 2(\cosh hD - 1)P(r) \\ &= 4\sinh^2 \frac{h}{2} D P(r),\end{aligned}$$

so that, symbolically,

$$4.2 \quad hD/2 = \sinh^{-1}(\frac{\delta}{2})^{\frac{1}{2}}.$$

Further,

$$\begin{aligned}\delta^2 P &= h^2 D^2 P + \left[(2\sinh \frac{1}{2} hD)^2 - h^2 D^2 \right] P \\ &= h^2 gP + \left[(\sinh \frac{1}{2} hD / \frac{1}{2} hD)^2 - 1 \right] h^2 gP\end{aligned}$$

by equation 4.1. Using 4.2, one obtains

$$4.3 \quad \delta^2 P = h^2 gP + h^2 \left\{ \left(\frac{\delta}{2} / \sinh^{-1}(\frac{1}{2} \delta)^{\frac{1}{2}} \right)^2 - 1 \right\} gP.$$

The operator in brackets may be expanded in a power series; when this is done, equation 4.3 reads

$$4.4 \quad \delta^2 P/h^2 = gP + \delta^2(gP)/12 - \delta^4(gP)/240 - \dots$$

(Equation 4.4 is derived in a more straightforward but laborious manner by E. Milne,¹³)

Consider now a function denoted by $\delta^{-2}(gP)$ whose second differences are gP ; in terms of such a function 4.4 can be written

$$4.5 \quad \delta^2 P/h^2 = \delta^{-2}[\delta^{-2}(gP) + gP/12 - \delta^2(gP)/240 + \dots],$$

from which is apparent that the functions

$$4.6 \quad P/h^2 \quad \text{and} \quad [\delta^{-2}(gP) + gP/12 - \delta^2(gP)/240 + \dots]$$

have the same second differences. The above definition of $\delta^{-2}(gP)$ does not determine it uniquely, for any function of the form $A + Br$, whose

13. E. Milne, Numerical Solutions of Differential Equations, pp.83, 84. (Wiley, New York, 1953.)

$$\begin{aligned} \frac{1}{2} \frac{d}{dt} \left(\frac{1}{2} \frac{d^2}{dt^2} \right) &= \frac{1}{2} \frac{d^3}{dt^3} \\ \frac{1}{2} \frac{d^2}{dt^2} &= \frac{1}{2} \frac{d^2}{dt^2} \\ \frac{1}{2} \frac{d}{dt} &= \frac{1}{2} \frac{d}{dt} \end{aligned}$$

$$\frac{1}{2} \frac{d}{dt} \left(\frac{1}{2} \frac{d^2}{dt^2} \right) = \frac{1}{2} \frac{d^3}{dt^3}$$

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The following is a list of the most important results of the theory of the differential equations of the second order.

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second differences vanish, may be added to a given $\delta^{-4}(gP)$ and the second differences of the sum will still be gP . In particular, A and B can be so chosen as to render the functions 4.6 equal for two adjacent tabular values of P; then those functions will be equal for all tabular values of the argument, wherefore

$$4.7 \quad P/h^2 = \delta^{-2}(gP) + gP/12 - \delta^2(gP)/240 + \dots$$

In practice, 4.7 may be truncated at the second term:

$$4.7a \quad P/h^2 = \delta^{-2}(gP) + gP/12$$

The error accumulated over a range of integration due to truncation can be estimated by summing $h^2\delta^2(gP)/240$ over that range; this was effected by differencing the leading and final differences of gP in that range (with due regard for sign) and multiplying by $h^2/240$.

In Table III, the equation $d^2P/dr^2 = P$ is solved and compared with the ascending solution $P = e^r$ to demonstrate the accuracy of the method.

Equation 4.7a was applied to the solution of 4.1 as follows. Values of P for $r=.02$ and $.04$ were calculated by the method of sec. 3 and entered in the P column (v. Table IV: the starting values are enclosed in parentheses). (The known value $P(n|0) = 0$ could not be used because $g_{nl}(0)$ is indeterminate.) From the entries under P, the corresponding values of P/h^2 , gP , and by means of 4.7a, $\delta^{-2}(gP)$ were computed. The difference of the last-mentioned was then entered in the $\delta^{-1}(gP)$ column, and added to $(gP)_{.04}$ to yield the next value of $\delta^{-1}(gP)$, which was in turn added to $\delta^{-2}(gP)_{.04}$ to give $\delta^{-2}(gP)_{.06}$.

To proceed with the solution, the value of $(gP)_{.06}$ was estimated and $(P/h^2)_{.06}$ calculated therefrom by 4.7a; this was then used to compute a value of $(gP)_{.06}$ which was compared with the estimated value. If different, the new value was used to calculate another value of P/h^2 , and this process was repeated until no further difference obtained.

The new value of gP was then added to the nearest $\delta^{-1}(gP)$ to yield the next value of $\delta^{-1}(gP)$, which was then added to the nearest $\delta^{-1}(gP)$ to get the next entry under $\delta^{-2}(gP)$, etc. The inward solution was conducted in a exactly similar manner.

At a change of the tabular interval, it was often necessary to interpolate a value of P halfway between two known values (e.g., $P(2s.25)$ Table IV); this was done by calculating $\delta^{-2}(gP)$ on the new interval for the known values, then calculating the required ordinate from

$$P(r) = \left\{ \delta^{-2}(gP)_{r-h} + \delta^{-2}(gP)_{r+h} \right\} / \left[\frac{2}{h^2} + \frac{5}{6} g(r) \right]$$

To demonstrate this, the numerator of the right hand side may be written, with the aid of 4.7, as

$$\begin{aligned} \delta^{-2}(gP)_{r-h} + \delta^{-2}(gP)_{r+h} &= [P(r+h) + P(r-h)]/h^2 - [(gP)_{r-h} + (gP)_{r+h}]/12 \\ &= \delta^2 P/h^2 + 2P/h^2 - \delta^2(gP)/12 - gP/16, \text{ by 4.4} \\ &= (2/h^2 + 5g/6)P, \text{ Q.E.D.} \end{aligned}$$

Within Tables IV and V are shown also the details of merging inward and outward solutions.

Table VI gives normalized values of the $P(n\ell|r)$ and their eigenvalues. Table VII compares the eigenvalues obtained with those found by Jucys² and ^{C.} ¹⁴ Torrance.

Fig. II is a plot of the $P(n\ell|r)$ vs. r compared with the corresponding functions obtained by Jucys.

H. Levy and ^{E.} ¹⁵ Baggott point out that to yield a solution correct to three significant figures, say, the numerical work must be carried to five.¹⁵ An extra figure was carried through^{out} in the calculation of $\delta^{-2}(gP)$ and gP to give rounding-off errors a place to accumulate harmlessly.¹⁶

14. C. Torrance, loc. primo cit., p. 389.

15. H. Levy and E. A. Baggott, Numerical Studies in Differential Equations, vol. I, p. 112. (Dover Publications, New York, 1960.)

16. H. Jeffreys and B. Jeffreys, op. cit., p. 277; also B. Hartree, Numerical Analysis, pp. 83-84. (Clarendon Press, Oxford, 1952.)

TABLE I

r	I(r)	B(r)	C(r)	W(r)
0.00	14.77	----	----	----
0.02	14.75	27.38	0.1414	0.9428
0.04	14.44	89.43	0.5760	3.922
0.06	14.13	70.76	1.002	4.007
0.08	13.71	53.08	1.520	3.826
0.10	13.30	38;61	1.974	3.646
0.12	12.84	28.66	2.368	3.523
0.14	12.40	20.00	2.659	3.234
0.16	11.95	14.59	2.872	3.098
0.18	11.48	9.839	3.060	2.795
0.20	11.10	6.999	3.167	2.637
0.25	10.15	2.524	3.224	2.096
0.30	9.355	1.531	3.230	2.014
0.35	8.664	+0.08489	3.116	1.383
0.40	8.088	-0.00394	3.028	1.243
0.45	7.592	+0.1065	2.924	1.170
0.50	7.176	0.2829	2.828	1.140
0.55	6.810	0.4478	2.730	1.120
0.60	6.498	0.5945	2.641	1.113 ₉₈
0.65	6.218	0.7175	2.529	1.114 ₃
0.70	5.974	0.7765	2.419	1.106
0.75	5.749	0.8145	2.294	1.101
0.80	5.550	0.8324	2.163	1.098
0.90	5.178	0.8027	1.881	1.081
1.0	4.839	0.7257	1.595	1.057
1.1	4.528	0.6596	1.359	1.059
1.2	4.245 ₈	0.5201	1.080	0.9840
1.3	3.997 ₉	0.4221	0.8729	0.9439
1.4	3.808 ₈	0.3372	0.7073	0.9115
1.5	3.608 ₃	0.2641	0.5632	0.8704
1.6	3.450 ₄	0.2056	0.4527	0.8376
1.7	3.277 ₂	0.1579	0.3550	0.7954
1.8	3.143 ₆	0.1211	0.2821	0.7622
1.9	2.992 ₇	0.09168	0.2205	0.7225
2.0	2.879 ₅	0.06966	0.1740	0.6922
2.1	2.754 ₂	0.05252	0.1353	0.6555
2.2	2.650 ₀	0.03953	0.1068	0.6285
2.3	2.531 ₆	0.02962	0.08290	0.5945
2.4	2.4501	0.02227-	0.06538	0.5710
2.6	2.2754	0.01352	0.04017	0.5205
2.8	2.131 ₉	0.00687	0.02455	0.4710
3.0	1.986 ₄	0.00395	0.01517	0.4377
3.2	1.866 ₀	0.00221	0.00933 ₅	0.4034
3.4	1.7590	0.00106	0.00565 ₅	0.3530
3.6	1.662 ₈	0.000697	0.00362 ₆	0.3455
3.8	1.576 ₅	0.000395	0.00227 ₈	0.3212
4.0	1.498 ₃	0.00022	0.00143 ₄	0.3005
4.5	1.332 ₅	0.00005 ₄	0.00045 ₃	0.2576
5.0	1.199 ₆	0.00001 ₄	0.00014 ₈	0.2272
5.5	1.090 ₈	0.00000 ₄	0.00004 ₉	0.2041
6.0	1.000 ₂	0.00000	0.00001 ₅	0.1667

Subscript numbers are only partially significant.

$W(r) = 1/r$, $I(r) = 6/r$, for $r \geq 6.0$.

FIGURE 1
COULOMB (I) AND EXCHANGE (W) TERMS
(HARTREE UNITS)

$$I \doteq \frac{6}{r}, \quad r \geq 6$$

$$W \doteq \frac{1}{r}, \quad r \geq 6$$

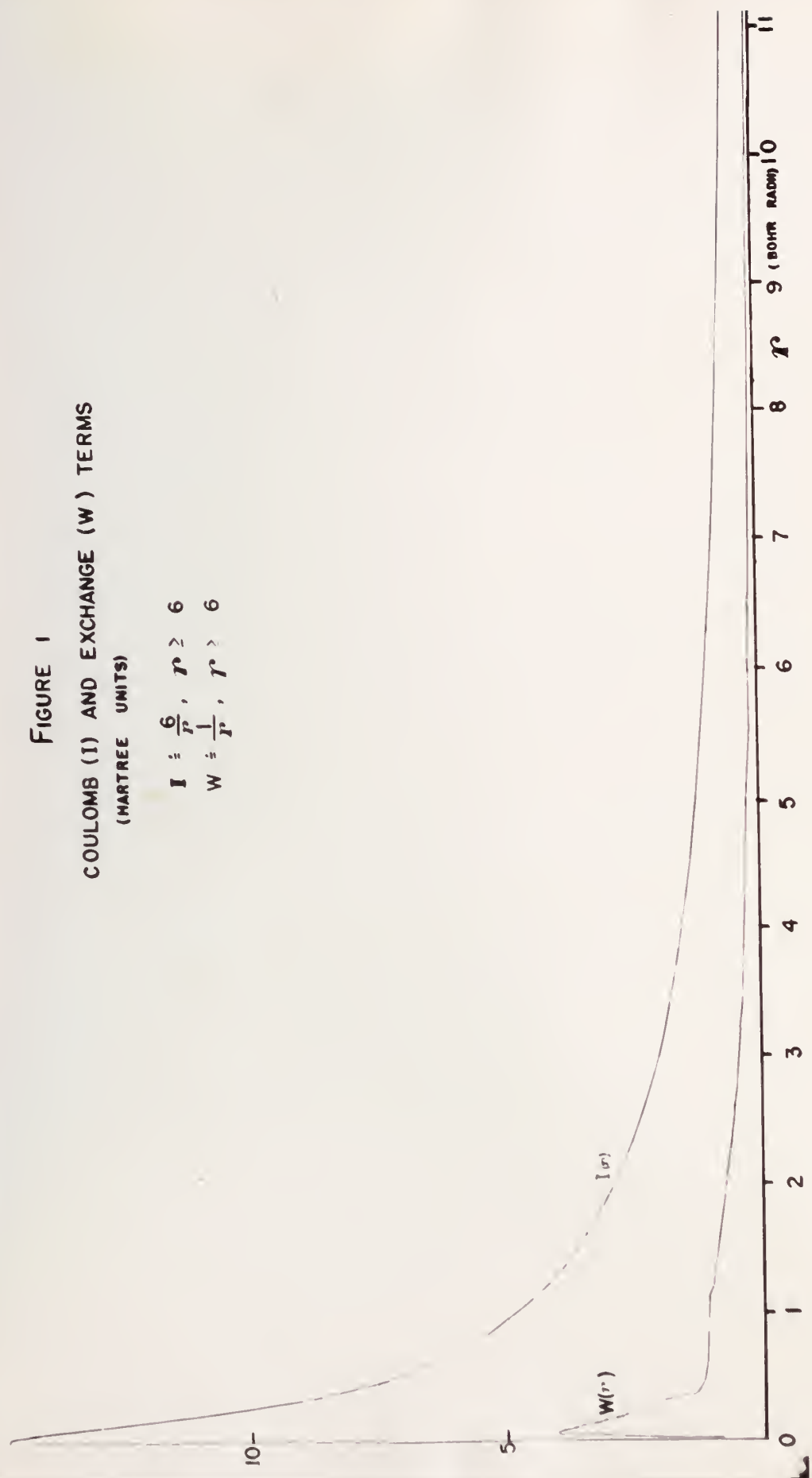


TABLE II

$$P(nl|r) = Ar^c(a_0 + a_1 r + a_2 r^2 + \dots), r \leq .04$$

nl	A	c	a_0	a_1	a_2	a_3	a_4	a_5
2s	-6.08804	1	1	-6	1.9896	-149.832	1580.395	---
2p	5.02513	2	1	-1/3	5.051	-75.0090	813.3513	-5171.58

$$P(nl|r) = Ar^b e^{-cr}(1 + a_1/r + a_2/r^2 + a_3/r^3 + \dots), r \geq 6.0$$

nl	A	b	c	a_1	a_2	a_3
2s	-5.3280	.7960611	1.256185	.0646194	-.00315757	---
2p	1.62085(-)	1.047824	.9543584	1.02157 ₁	.547399	.0134968

TABLE III

Numerical solution of $P = P$, compared with ascending solution $P = e^r$.

r	$\delta^{-2}P$	$\delta^{-1}P$	P	100P	e^r	error
.00	99.916		(1.0000 [*])	(100.00)	1.0000	.0000
.1	110.428	10.511	(1.1052)	(110.52)	1.1052	0
.2	122.044	11.616	1.222	122.15	1.2214	1
.3	134.882	12.838	1.350	134.90	1.3499	0
.4	149.070	14.188	1.492	149.19	1.4918	1
.5	164.750	15.680	1.640	164.89	1.6487	2
.6	182.079	17.329	1.822	182.23	1.8223	0
.7	201.230	19.151	2.014	201.40	2.0138	2
.8	222.395	21.165	2.226	222.58	2.2255	3
.9	245.786	23.391	2.460	245.09	2.4596	3
1.0	271.637	25.851	2.719	271.86	2.7183	.0003

* Parenthesized entries are "starting entries"

TABLE IV

Solution of $d^2P/dr^2 = gP$ for 2s case, unnormalized. $2E_{2s} = -1.5780$.

r	$\delta^2(gP)$	$\delta^1(gP)$	(gP)	2500P	g	P
0.02	(275.137)	(207.434)	(61.647)	(270.00)	-570.8020	(0.10800)
.04	(482.571)	154.382	(53.052)	(478.15)	277.3820	(0.19126)
.06	636.953	109.255	45.127	633.19	178.4720	.25328
.08	746.208	70.986	38.269	743.02	128.7620	.29721
.10	817.194	38.692	32.294	814.50	99.1220	.32580
.12	855.886	+11.447	27.245	853.62	79.7920	.34145
.14	867.333	-11.332	22.779	865.43	65.8020	.34617
.16	856.001	30.372	19.040	854.41	55.7120	.34176
.18	825.629	46.104	15.732	824.32	47.7120	.32973
.20	779.525	59.021	12.917	778.449	41.4820	.31138
.22	720.504	69.433	10.412	719.64	36.1720	.
.24	651.071	-77.766	8.333	650.377	32.0320	
.26	573.305		-6.633	572.752	-28.9520	
.24	2602.20	-151.61	-8.333	⁴ 10 P 2601.51	-32.0320	
.25	2450.59	+159.04	7.43	2449.97	30.3120	.24500
.26	2291.56		-6.63	2291.01	-28.9520	
.20	125.6282	-27.0105	-12.9166	400P 124.5518	-41.4820	.31138
.25	98.6177	34.4368	7.4263	97.9988	30.3120	.24500
.30	64.1809	38.2275	3.7907	63.865	23.7420	.15966
.35	+25.9534	39.4008	-1.1733	+25.856	18.1520	+0.06464
.40	-13.4474	38.9071	+0.4937	-13.406	14.7320	-0.0335 ₁₅
.45	52.3545	37.3076	1.5995	52.221	12.2520	.130550
.50	89.6621	34.9921	2.3155	89.469	10.3520	.22367
.55	124.6542	-32.2356	2.7565	124.42	8.8620	.31105
.60	156.8898		2.9965	-156.64	-7.6520	-0.39160

Sign is indicated only at the head and foot of a column, and at a change.

TABLE IV (Cont.)						
r	δ^{-2} (gP)	δ^{-1} (gP)	gP	400P	g	P
0.60	-156.8898		2.9965	-156.64	-7.6520	-.39160
		-29.2391				
.65	186.1289		3.1003	185.87	6.6720	.46468
		26.1388				
.70	212.2677		3.0900	212.010	5.8300	.53003
		23.0488				
.75	235.3165		3.0124	235.07	5.1260	-.58768
		-20.0364				
.80	-255.3529		2.8815	-255.113	-4.5180	
				100P		
.70	-53.2603		3.0901	-53.0028	-5.8300	-.530025
		-10.7581				
.80	64.0184		2.8815	63.7783	4.5180	.637783
		7.8766				
.90	71.8950		2.5526	71.682	3.5610	.71682
		5.3240				
1.00	77.2190		2.2009	77.036	2.8570	.77036
		3.1231				
1.1	80.3421		1.2645	80.237	1.5760	.80237
		1.8586				
1.2	82.2007		1.5577	82.071	1.8980	.82071
		-0.3009				
1.3	82.5016		1.2730	82.396	1.5450	.82396
		+0.9721				
1.4	81.5295		0.9757	81.448	1.1980	.81448
		1.9478				
1.5	79.5817		.7522	79.519	.9460	.79519
		2.7000				
1.6	76.8817		.5348	76.837	.6960	.76837
		3.2348				
1.7	73.6469		.3806	73.615	.5170	.73615
		3.6154				
1.8	70.0315		.2282	70.012	.3260	.70012
		3.8436				
1.9	66.1879		.1310	66.177	.1980	.66177
		3.9746				
2.0	62.2133		+.0292	62.211	-.0470	.62211
		4.0038				
2.1	58.2095		-.0355	58.212	+.0610	.58212
		3.9683				
2.2	54.2412		.0901	54.249	.01660	.54249
		3.8782				
2.3	50.3630		.1184	50.373	.2350	.50373
		+3.7598				
2.4	-46.6032		-.1566	-46.616	+.3360	-.46616

Sign is indicated only at the head and foot of a column, and at a change.

TABLE IV (Cont.)

r	$\delta^{-2}(gP)$	$\delta^{-1}(gP)$	gP	25P	g	P
2.2	-13.5548		-.0901	-13.5623	+0.1660	-0.54249
		+1.9138				
2.4	11.6410		.1566	11.6540	.3360	.46616
		1.7572				
2.6	9.8838		.1873	9.899	.4730	.39596
		1.5699				
2.8	8.3139		.1980	8.330	.5943	.33320
		1.3719				
3.0	6.9420		.1879	6.958	.6750	.27832
		1.1840				
3.2	5.7580		.1739	5.772	.7530	.23088
		1.0101				
3.4	4.7479		.1639	4.762	.8606	.19048
		0.8462				
3.6	3.9017		.1377	3.913	.8797	.15652
		.7085				
3.8	3.1932		.1193	3.203	.9311	.12812
		.5892				
4.0	-2.6040		-.1018	-2.612	.9740	-.10448

100P

3.4	-19.034		-.164	-19.048	+ .8606	-.19048
		1.773				
3.5	17.261		.152	17.274	.8814	.17274
		1.021				
3.6	-15.641		-.138	-15.652	.8797	-.15652

4P

6.5	-0.496244		-0.161813	-0.509728	1.2698	-0.127432
		-0.377531				
6.0	.873775		.279135	.897036	1.2447	-.224259
		.656666				
5.5	1.53044		.45850	1.5686	1.1692	
		1.11517				
5.0	2.64561		.76055	2.7090	1.1230	
		1.87572				
4.5	4.52133		1.22676	4.6236	1.0613	
		3.10248				
4.0	7.62381		1.89484	7.7817	0.9740	
		-4.99732				
3.5	-12.62113		-2.8330	-12.857	.8814	

Outward Sol'n.

Inward Sol'n.

Conv's'n. Factor

Conv. I. S.

3.5	-.17274	-12.857	.01343548	-.17274
4.0	-.10448	-7.7817		-.10455

Normalizing factor for this solution: 0.990624

1	2	3	4	5	6
7	8	9	10	11	12
13	14	15	16	17	18
19	20	21	22	23	24
25	26	27	28	29	30
31	32	33	34	35	36
37	38	39	40	41	42
43	44	45	46	47	48
49	50	51	52	53	54
55	56	57	58	59	60
61	62	63	64	65	66
67	68	69	70	71	72
73	74	75	76	77	78
79	80	81	82	83	84
85	86	87	88	89	90
91	92	93	94	95	96
97	98	99	100	101	102
103	104	105	106	107	108
109	110	111	112	113	114
115	116	117	118	119	120
121	122	123	124	125	126
127	128	129	130	131	132
133	134	135	136	137	138
139	140	141	142	143	144
145	146	147	148	149	150
151	152	153	154	155	156
157	158	159	160	161	162
163	164	165	166	167	168
169	170	171	172	173	174
175	176	177	178	179	180
181	182	183	184	185	186
187	188	189	190	191	192
193	194	195	196	197	198
199	200	201	202	203	204
205	206	207	208	209	210
211	212	213	214	215	216
217	218	219	220	221	222
223	224	225	226	227	228
229	230	231	232	233	234
235	236	237	238	239	240
241	242	243	244	245	246
247	248	249	250	251	252
253	254	255	256	257	258
259	260	261	262	263	264
265	266	267	268	269	270
271	272	273	274	275	276
277	278	279	280	281	282
283	284	285	286	287	288
289	290	291	292	293	294
295	296	297	298	299	300
301	302	303	304	305	306
307	308	309	310	311	312
313	314	315	316	317	318
319	320	321	322	323	324
325	326	327	328	329	330
331	332	333	334	335	336
337	338	339	340	341	342
343	344	345	346	347	348
349	350	351	352	353	354
355	356	357	358	359	360
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439	440	441	442	443	444
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463	464	465	466	467	468
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475	476	477	478	479	480
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487	488	489	490	491	492
493	494	495	496	497	498
499	500	501	502	503	504
505	506	507	508	509	510
511	512	513	514	515	516
517	518	519	520	521	522
523	524	525	526	527	528
529	530	531	532	533	534
535	536	537	538	539	540
541	542	543	544	545	546
547	548	549	550	551	552
553	554	555	556	557	558
559	560	561	562	563	564
565	566	567	568	569	570
571	572	573	574	575	576
577	578	579	580	581	582
583	584	585	586	587	588
589	590	591	592	593	594
595	596	597	598	599	600
601	602	603	604	605	606
607	608	609	610	611	612
613	614	615	616	617	618
619	620	621	622	623	624
625	626	627	628	629	630
631	632	633	634	635	636
637	638	639	640	641	642
643	644	645	646	647	648
649	650	651	652	653	654
655	656	657	658	659	660
661	662	663	664	665	666
667	668	669	670	671	672
673	674	675	676	677	678
679	680	681	682	683	684
685	686	687	688	689	690
691	692	693	694	695	696
697	698	699	700	701	702
703	704	705	706	707	708
709	710	711	712	713	714
715	716	717	718	719	720
721	722	723	724	725	726
727	728	729	730	731	732
733	734	735	736	737	738
739	740	741	742	743	744
745	746	747	748	749	750
751	752	753	754	755	756
757	758	759	760	761	762
763	764	765	766	767	768
769	770	771	772	773	774
775	776	777	778	779	780
781	782	783	784	785	786
787	788	789	790	791	792
793	794	795	796	797	798
799	800	801	802	803	804
805	806	807	808	809	810
811	812	813	814	815	816
817	818	819	820	821	822
823	824	825	826	827	828
829	830	831	832	833	834
835	836	837	838	839	840
841	842	843	844	845	846
847	848	849	850	851	852
853	854	855	856	857	858
859	860	861	862	863	864
865	866	867	868	869	870
871	872	873	874	875	876
877	878	879	880	881	882
883	884	885	886	887	888
889	890	891	892	893	894
895	896	897	898	899	900
901	902	903	904	905	906
907	908	909	910	911	912
913	914	915	916	917	918
919	920	921	922	923	924
925	926	927	928	929	930
931	932	933	934	935	936
937	938	939	940	941	942
943	944	945	946	947	948
949	950	951	952	953	954
955	956	957	958	959	960
961	962	963	964	965	966
967	968	969	970	971	972
973	974	975	976	977	978
979	980	981	982	983	984
985	986	987	988	989	990
991	992	993	994	995	996
997	998	999	1000	1001	1002

TABLE V

Solution of $dP/dr = g_P$, for 2p case, with $2E = -.9108$; unnormalized.

r	$\delta^{-2}(g_P)$	$\delta^{-1}(g_P)$	g_P	2500P	g	P
0.02	4.262		8.857	5.000	4428.5308	0.00200
		15.013				
.04	19.275		7.745	19.920	971.9508	.007968
		22.758				
.06	42.033		6.414	42.567	376.7164	.017027
		29.172				
.08	71.205		5.246	71.642	183.0708	.028657
		34.418				
.10	105.623		4.248	105.98	100.2108	.042392
		38.666				
.12	144.289		3.379	144.57	58.2968	.057828
		42.045				
.14	186.334		2.654	186.56	35.5716	.074624
		44.699				
.16	231.033		2.011	231.20	21.7458	.092480
		46.710				
.18	277.743		1.484	277.87	13.3492	.11148
		48.194				
.20	325.937		1.024	326.022	7.8508	.130409
		49.218				
.22	375.155		0.673	375.211	4.4831	.150084
		49.891				
.24	425.046		+0.344	425.075	2.02302	.170030
		50.235				
.26	475.281		-0.006	475.281	-0.0334	.190112
				$10^4 P$		
.24	1700.27		+0.34	1700.30	+2.02302	.17003
		100.34				
.25	1800.61		+ .18	1800.62	+1.0208	.180062
		100.52				
.26	1901.12		-0.006	1901.12	-0.0334	.190112
				400P		
.20	52.0783		1.0238	52.1636	7.8508	.130409
		19.9312				
.25	72.0095		+0.1838	72.0248	+1.0208	.180062
		20.1150				
.30	92.1245		-0.5035	92.083	-2.1870	.23021
		19.6115				
.35	111.736		.696	111.678	2.4927	.27920
		18.916				
.40	130.652		.946	130.57	2.8992	.32643
		17.970				
.45	148.622		1.130	148.53	3.0427	.37133
		16.840				
.50	165.462		1.248	165.36	3.0192	.41340
		15.592				
.55	181.054		1.320	180.94	2.9176	.45235
		14.272				
.60	195.326		1.349	195.21	2.7636	.48803

Sign is indicated only at the head and foot of a column, and at changes.

TABLE V (Cont.)

r	$\delta^{-2}(\text{gP})$	$\delta^{-1}(\text{gP})$	gP	400P	g	P
0.60	195.326		-1.349	195.21	-2.7636	0.48803
		12.923				
.65	208.249		1.356	208.14	2.6055	.52035
		11.567				
.70	219.816		1.327	219.705	2.4156	.54926
		10.240				
.75	230.056		1.286	229.95	2.2376	.57488
		8.954				
.80	239.010		-0.659	238.955	-1.1032	.59739
				100P		
.70	55.0369		-1.3268	54.9263	-2.4156	0.54926 ₃
		4.7568				
.80	59.7937		0.6590	59.7388	1.1032	.59738 ₈
		4.0978				
.90	63.8915		1.1223	63.798	1.7591	.63798
		2.9755				
1.0	66.8670		1.0179	66.782	1.5242	.66782
		1.9576				
1.1	68.8246		0.4061	68.791	0.5903	.68791
		1.5515				
1.2	70.3761		.8270	70.307	1.1763	.70307
		+0.7245				
1.3	71.1006		.7309	71.040	1.0288	.71040
		-0.0064				
1.4	71.0942		.6002	71.044	0.8448	.71044
		.6066				
1.5	70.4876		.5102	70.445	.7243	.70445
		1.1168				
1.6	69.3708		.4035	69.337	.5819	.69337
		1.5203				
1.7	67.8505		.3338	67.823	.4922	.67823
		1.8541				
1.8	65.9964		.2480	65.976	.3759	.65976
		2.1021				
1.9	63.8943		.1988	63.878	.3112	.63878
		2.3009				
2.0	61.5934		.1319	61.582	.2142	.61582
		2.4328				
2.1	59.1606		.0903	59.153	.1527	.59153
		2.5231				
2.2	56.6375		.0498	56.6334	.0880	.56633 ₄
		-2.5729				
2.3	54.0646		-.0292	54.062	-.0541	.54062
		-2.6021				
2.4	51.4625		+.0082	51.4632	+.0160	.51463 ₂

TABLE V (Cont.)

r	$\delta^{\gamma}(gP)$	$\delta^{\gamma}(gP)$	gP	25P	g	P
2.2	14.1625		-.0498	14.1584	-0.0880	0.566334
		-1.2974				
2.4	12.8651		+.0082	12.8658	+.0160	.514632
		1.2892				
2.6	11.5759		.0471	11.580	.1017	.46320
		1.2421				
2.8	10.3338		.0754	10.340	.1822	.41360
		1.1667				
3.0	9.1671		.0844	9.174	.2300	.36696
		1.0823				
3.2	8.0848		.0910	8.092	.2811	.32368
		0.9913				
3.4	7.0935		.1041	7.1022	.3664	.28409
		.8872				
3.6	6.2063		.0912	6.2139	.3668	.24856
		.7960				
3.8	5.4103		.0872	5.418	.4024	.21672
		-.7088				
4.0	4.7015		.0813	4.7083	.4318	.18833
				100P		
3.4	28.400		.104	28.409	.3664	.28409
		-1.8260				
3.5	26.574		.100	26.582	.3775	.26582
		-1.726				
3.6	24.848		.091	24.856	.3668	.24856
				4P		
6.5	0.66379		0.10933	0.672900	0.6499	0.168225
		0.33315				
6.0	0.99694		.15987	1.01026	.6330	.252565
		.49302				
5.5	1.48996		.21415	1.5078	.5681	
		.70717				
5.0	2.19713		.29762	2.2219	.5358	
		1.00479				
4.5	3.20192		.39865	3.2351	.4929	
		1.40344				
4.0	4.60536		.50167	4.6472	.4318	
		1.90511				
3.5	6.51047		.61930	6.5621	.3775	

	Outward Sol'n.	Inward Sol'n.	Conv's'n Factor	Converted I. S.
3.5	0.26582	6.5621	.0405084	0.26582
4.0	.18833	4.6472		.18825

Normalization factor for this solution: 1.000315

1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30	31	32	33	34	35
36	37	38	39	40	41	42
43	44	45	46	47	48	49
50	51	52	53	54	55	56
57	58	59	60	61	62	63
64	65	66	67	68	69	70
71	72	73	74	75	76	77
78	79	80	81	82	83	84
85	86	87	88	89	90	91
92	93	94	95	96	97	98
99	100	101	102	103	104	105
106	107	108	109	110	111	112
113	114	115	116	117	118	119
120	121	122	123	124	125	126
127	128	129	130	131	132	133
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141	142	143	144	145	146	147
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155	156	157	158	159	160	161
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260	261	262	263	264	265	266
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386	387	388	389	390	391	392
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414	415	416	417	418	419	420
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449	450	451	452	453	454	455
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463	464	465	466	467	468	469
470	471	472	473	474	475	476
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505	506	507	508	509	510	511
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519	520	521	522	523	524	525
526	527	528	529	530	531	532
533	534	535	536	537	538	539
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554	555	556	557	558	559	560
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603	604	605	606	607	608	609
610	611	612	613	614	615	616
617	618	619	620	621	622	623
624	625	626	627	628	629	630
631	632	633	634	635	636	637
638	639	640	641	642	643	644
645	646	647	648	649	650	651
652	653	654	655	656	657	658
659	660	661	662	663	664	665
666	667	668	669	670	671	672
673	674	675	676	677	678	679
680	681	682	683	684	685	686
687	688	689	690	691	692	693
694	695	696	697	698	699	700
701	702	703	704	705	706	707
708	709	710	711	712	713	714
715	716	717	718	719	720	721
722	723	724	725	726	727	728
729	730	731	732	733	734	735
736	737	738	739	740	741	742
743	744	745	746	747	748	749
750	751	752	753	754	755	756
757	758	759	760	761	762	763
764	765	766	767	768	769	770
771	772	773	774	775	776	777
778	779	780	781	782	783	784
785	786	787	788	789	790	791
792	793	794	795	796	797	798
799	800	801	802	803	804	805
806	807	808	809	810	811	812
813	814	815	816	817	818	819
820	821	822	823	824	825	826
827	828	829	830	831	832	833
834	835	836	837	838	839	840
841	842	843	844	845	846	847
848	849	850	851	852	853	854
855	856	857	858	859	860	861
862	863	864	865	866	867	868
869	870	871	872	873	874	875
876	877	878	879	880	881	882
883	884	885	886	887	888	889
890	891	892	893	894	895	896
897	898	899	900	901	902	903
904	905	906	907	908	909	910
911	912	913	914	915	916	917
918	919	920	921	922	923	924
925	926	927	928	929	930	931
932	933	934	935	936	937	938
939	940	941	942	943	944	945
946	947	948	949	950	951	952
953	954	955	956	957	958	959
960	961	962	963	964	965	966
967	968	969	970	971	972	973
974	975	976	977	978	979	980
981	982	983	984	985	986	987
988	989	990	991	992	993	994
995	996	997	998	999	1000	1001

Normalized solutions of the $2s$ and $2p$ radial equations.

r	$P(2s r)$	$P(2p r)$	r	$P(2s r)$	$P(2p r)$
0.00	0.000	0.000	1.7	-0.729	0.678
.02	.107	.002	1.8	.694	.660
.04	.190	.008	1.9	.656	.639
.06	.251	.017	2.0	.612	.616
.08	.294	.029	2.1	.577	.592
.10	.323	.042	2.2	.537	.567
.12	.338	.058	2.3	.499	.541
.14	.343	.075	2.4	.462	.515
.16	.339	.093	2.6	.392	.463
.18	.327	.111	2.8	.330	.414
.20	.309	.130	3.0	.276	.367
.25	.243	.180	3.2	.229	.324
.30	.158	.230	3.4	.189	.284
.35	+0.064	.279	3.6	.155	.249
.40	-0.033	.327	3.8	.127	.217
.45	.129	.371	4.0	.104	.188
.50	.222	.414	4.5	.062	.131
.55	.308	.453	5.0	.036	.090
.60	.388	.488	5.5	.021	.061
.65	.460	.521	6.0	.012	.041
.70	.525	.550	6.5	.007	.027
.75	.582	.575	7.0	.004	.018
.80	.632	.598	7.5	.002	.012
.90	.710	.638	8.0	.001	.008
1.0	.763	.668	9.0	.0004	.003
1.1	.795	.688	10.0	.0001	.001
1.2	.813	.703	11.0	.0000	.0001
1.3	.816	.711	12.0	.0000	.0000
1.4	.807	.711			
1.5	.788	.705			
1.6	-0.761	0.694			

Asymptotic expansions are given in Table II.

TABLE VII

Comparison of eigenvalues arising from various exchange terms.

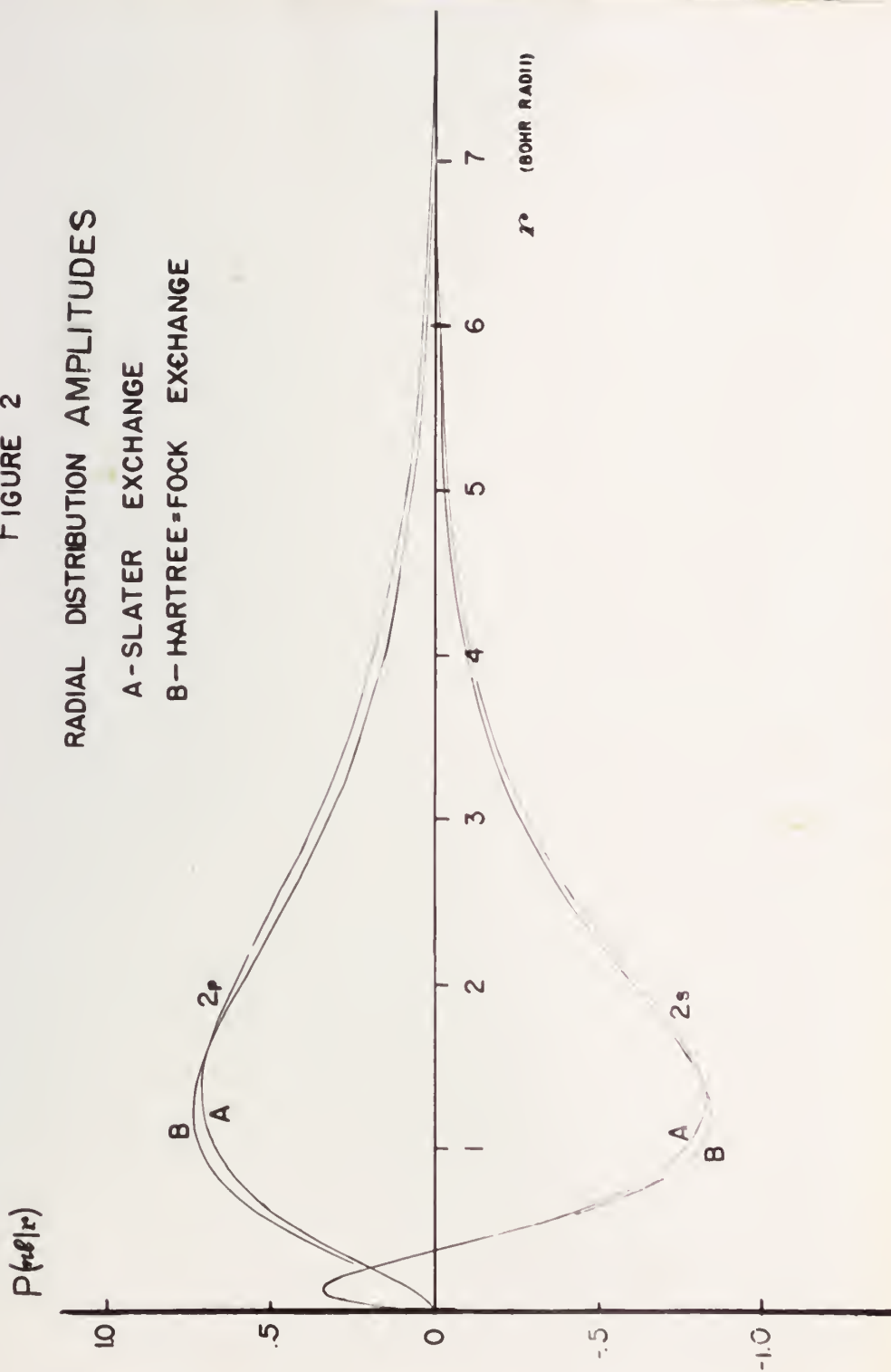
Exchange	$-2E_{1b}$	$-2E_{1s}$
None ⁷	0.6435	1.2454
Hartree-Fock ²	0.9569	1.8831
Slater	0.9168	1.5780

FIGURE 2

RADIAL DISTRIBUTION AMPLITUDES

A - SLATER EXCHANGE

B - HARTREE-FOCK EXCHANGE



5. Conclusions--The wave functions tabulated in Table VI are not self-consistent on the usual criterion that the integrals $\int_0^r dr P^2(nl|r)$ calculated from starting and resulting functions shall differ less than $0.02/(2l+1)$ ¹⁹. Refinement to self-consistency is necessary to realize the full accuracy of which Slater's method may be capable. However, the functions represent the first phase of such a calculation. Moreover, since they differ little from Jucys' functions (which by virtue of arising from a variational principle represent the "best" one-electron approximation embodying the Pauli principle), they must possess considerable accuracy. Therefore, since they arise from a plausible unipotential, they may be used as they stand in calculations requiring unipotential.

The method is not more tedious or time-consuming than the Hartree-Fock method (indeed, it is less so by reason of the unipotential); and yields a more accurate set of wave functions than the Hartree⁷ method, for the quadrivalent carbon atom at least. Nevertheless, carrying the solution through to self-consistency is a difficult project for the lone worker; especially so, because the self-consistent procedure is not necessarily convergent,¹⁹ so that various devices must be used to obtain convergence.

19. G. Pratt, Phys. Rev., 88, 1219, '52.

APPENDIX I

An extensive literature exists on the Hartree-Fock equations.¹⁷ As modified by Dirac,⁴ these equations for the atomic orbitals read:

$$(a) -\left[\frac{1}{2}\nabla^2 + \frac{Z}{r_1}\right]u_i(1) + u_i(1)\sum_{j=1}^Z \int d\tau_2 u_j^*(2) \frac{1}{r_{12}} u_j(2) - \sum_{j=1}^Z u_j(1) \int d\tau_2 u_j^*(2) \frac{1}{r_{12}} u_i(1) = E_i u_i(1),$$

$i = 1, 2, \dots, Z.$

To put this in the form of a Schrödinger equation, Slater¹ rewrites the exchange term, i.e., the second summation, thus:

$$(b) \sum_{j=1}^Z \int d\tau_2 u_j(1) u_j^*(2) \frac{1}{r_{12}} u_i(2) = \sum_{j=1}^Z \int d\tau_2 \frac{u_i^*(1) u_j(1) u_i(1) u_j^*(2)}{|u_i(1)|^2} \frac{1}{r_{12}} u_i(2)$$

This device puts (a) in the Schrödinger form with an effective potential for the ith electron given by

$$(c) -\frac{Z}{r_1} + \sum_{j=1}^Z \int d\tau_2 u_j^*(2) \frac{1}{r_{12}} u_j(2) - \sum_{j=1}^Z \int d\tau_2 \frac{u_i^*(1) u_j(1) u_j^*(2) u_i(2)}{|u_i(1)|^2 r_{12}}.$$

The terms of this potential are interpreted physically by Slater:^{1, 18} $-\frac{Z}{r}$ is simply the electrostatic field of the nucleus; the first summation accounts for the screening effect of the "charge cloud" of electrons surrounding the nucleus, for $u_j^*(2)u_j(2)$ is simply the Schrödinger charge density for the jth electron, and the integral its Coulomb effect; the second summation provides "...correction due to the fact that the electron really does not act on itself."¹⁸ The exchange term alone of the effective potential is not the same for all electrons; to render it so, Slater strikes a mean of exchange terms weighted with the probability that the electron with the coordinates (1) is in the state i:

$$u_i^*(1) u_i(1) / \sum_{j=1}^Z u_j^*(1) u_j(1)$$

17. J. C. Slater, Phys. Rev., 35, 210, '30;
 V. Fock, Z. Physik, 61, 126, '30;
 D. and W. Hartree, Proc. Roy. Soc., A150, 9, '35;
 V. also footnotes 1, 5, and 11, as well as references given by Slater, loc. primo cit.
 18. Slater, Phys. Rev., 82, 538, '51.

18. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function and that its value is zero.

20. In the second part of the paper, we consider the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function and that its value is zero.

22. In the third part of the paper, we consider the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function and that its value is zero.

24. In the fourth part of the paper, we consider the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function and that its value is zero.

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The result is

$$\sum_{j=1}^Z \sum_{k=1}^Z \int d\tau_{12} u_k^*(1) u_j^*(2) \frac{1}{r_{12}} u_j(1) u_k(2) / \sum_{j=1}^Z |u_j(1)|^2$$

However, in view of the insensitivity of the core electrons to the presence of other electrons, (v. sec. 1, p.2), a better approximation to the truth obtains if the valence electrons are supposed to move in an exchange which results from averaging (b) over them alone. With the indices as assigned in sec. 2, this exchange is

$$\sum_{j=3}^Z \sum_{k=1}^Z \int d\tau_{12} u_j^*(1) u_k^*(2) \frac{1}{r_{12}} u_k(1) u_j(2) / \sum_{j=3}^Z |u_j(1)|^2 = \sum_{j=3}^Z \sum_{k=1}^Z I_{jk} / \sum_{j=3}^Z |u_j(1)|^2.$$

The denominator works out to $[P^2(2s|r) + 3P^2(2p|r)] / 4\pi r^2$ while the summation written out in full is

$$(I_{13} + I_{33} + I_{34} + I_{35} + I_{36}) + (I_{14} + I_{15} + I_{16} + I_{34} + I_{35} + I_{36} + I_{44} + I_{55} + I_{66} + 2I_{45} + 2I_{46} + 2I_{56}).$$

The sums in parentheses are $B(r)/4\pi$ and $C(r)/4\pi$ respectively, essentially the functions tabulated in Table I. Combining the above results yields

$$W(r) = [B(r) + C(r)] / [P^2(2s|r) + 3P^2(2p|r)] \cdot \frac{1}{r}.$$

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$$\frac{1}{2} \left(\frac{1}{2} + \frac{1}{2} \right) = 1$$

Evaluation of $I_c(r)$ —By definition

$$I_c(r) = \int d\tau_1 u_1^*(1) u_c^*(2) \cdot (1/r_{12}) u_c(2) u_c(1) \quad .$$

Now

$$\begin{aligned} & u_1^*(1) u_c^*(2) u_c(2) u_c(1) \\ &= (3/16\pi^2) P_1'(\xi_1) P_1'(\xi_2) e^{i(\varphi_2 - \varphi_1)} P(1s|r_1) P(2p|r_1) P(1s|r_2) P(2p|r_2) / r_1^2 r_2^2, \end{aligned}$$

where $\xi_i = \cos \theta_i$, and the sines have been written in terms of the associated Legendre polynomials $P_1'(\cos \theta)$.

To perform the integrations, using the orthogonality properties of the exponentials and Legendre polynomials, it is necessary to invoke the following expansions, given by A. Sommerfeld in Partial Differential Equations in Physics, Pages 134 ff.; (Academic Press, New York, 1949.)

$$\begin{aligned} 1/r_{12} &= (1/r_1) \sum_{n=0}^{\infty} P_n(\cos \gamma) (r_2/r_1)^n, \quad r_2 < r_1, \\ &= (1/r_2) \sum_{n=0}^{\infty} P_n(\cos \gamma) (r_1/r_2)^n, \quad r_1 < r_2, \\ P_n(\cos \gamma) &= \sum_{m=-n}^n P_n^{im}(\xi_1) P_n^{im}(\xi_2) e^{im(\varphi_1 - \varphi_2)} (n-|m|)! / (n+|m|)!, \end{aligned}$$

where $\cos \gamma = \vec{r}_1 \cdot \vec{r}_2 / r_1 r_2$, and $P_n(\xi)$ is the Legendre polynomial of degree n .

The volume of the integration must be divided into two regions, one with $r_2 < r_1$, and the other with $r_1 < r_2$, in order that the above expansions shall converge uniformly.

The angular integration for the region $r_2 < r_1$ reads:

$$\begin{aligned} & \frac{1}{r_1} \sum_{n=0}^{\infty} \sum_{m=-n}^n \int_0^{2\pi} \int_{-1}^1 d\xi_2 d\varphi_2 P_1'(\xi_1) P_1'(\xi_2) e^{i(\varphi_2 - \varphi_1)} (r_2/r_1)^n P_n^{im}(\xi_1) P_n^{im}(\xi_2) e^{im(\varphi_1 - \varphi_2)} (n-|m|)! / (n+|m|)! \\ &= \sum_{n=0}^{\infty} \int_{-1}^1 d\xi_2 P_1'(\xi_2) P_1'(\xi_1) (2\pi/r_1) (r_2/r_1)^n P_n^{im}(\xi_1) P_n^{im}(\xi_2) (n-1)! / (n+|m|)! \\ &= (2\pi/r_1) (r_2/r_1) [P_1'(\xi_1)]^2, \text{ upon } \text{our} \text{ using the orthogonality properties, To} \end{aligned}$$

average this over angles, it was multiplied by $(1/4\pi) d\xi_1 d\varphi_1$ and integrated over all angles:

$$\frac{1}{4\pi} \frac{4\pi}{3r_1} \left(\frac{r_2}{r_1} \right) \int_{-1}^1 \int_0^{2\pi} d\xi_1 d\varphi_1 [P_1'(\xi_1)]^2 = \frac{4\pi}{9r_1} (r_2/r_1) \quad .$$

For the other region, the rôles of r_1 and r_2 must be reversed.

The integral $I_{10}(r)$ now becomes

$$\frac{P(1s|r_1) P(2p|r_1)}{12\pi r_1^2} \left[\frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 P(1s|r_1) P(2p|r_2) + r_1 \int_{r_1}^{\infty} \frac{dr_2 P(1s|r_1) P(2p|r_2)}{r_2^2} \right]$$

$$= \frac{P(1s|r_1) P(2p|r_1)}{12\pi r_1^2} \frac{1}{r_1} Y_0(1s, 2p; r_1)$$

The results of such evaluation are given in sec. 2 above.



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